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Hiromu Taguchi[a]; Norio Kunieda[a]; Masayoshi Kinoshita[a]
[a] Department of Applied Chemistry Faculty of Engineering, Osaka City University, Sumiyoshi-ku, Osaka, Japan

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Vinyl Polymerization Initiated by the Cycloamylose/Metal Ion System in Water

HIROMU TAGUCHI, NORIO KUNIEDA, and MASAYOSHI KINOSHITA

Department of Applied Chemistry
Faculty of Engineering
Osaka City University
Sumiyoshi-ku, Osaka, Japan

ABSTRACT

The polymerization of vinyl monomers, methyl methacrylate (MMA), benzyl methacrylate (BMA), styrene, and acrylonitrile has been carried out using the cycloamylose/metal ion systems in water. We have found that the α-, β-, and γ-cyclodextrins have an ability to initiate the polymerization of MMA and BMA in combination with Cu(II) or Fe(III) ions.

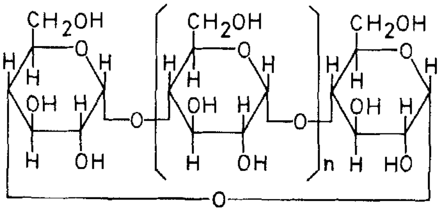
INTRODUCTION

It has been reported that polysaccharides, such as cellulose and starch, have an ability to initiate the polymerization of methyl methacrylate (MMA) in water [1]. The addition of Cu(II) ion and/or carbon tetrachloride to the starch/water/MMA system has resulted in the acceleration of polymerization. In this polymerization process the hydrophobic area formed by polysaccharides in water have been considered to play an important role, and an initiation mechanism which proceeds through the initial incorporation of MMA into the hydrophobic areas has been proposed [2].

These facts have prompted us to examine the polymerization of some vinyl monomers initiated by cycloamyloses (cyclodextrin compounds) which possess an ability to include specifically various sorts of organic compounds into their hydrophobic hole in water [3].

We have now found that cycloamyloses can serve as initiators of polymerization of MMA and benzyl methacrylate (BMA) in water in combination with some metal ions such as Cu(II) and Fe(III).

In the present paper we would report the results of the polymerizations of MMA, BMA, styrene (St), and acrylonitrile (AN) by using α-, β-, and γ-cyclodextrins in the presence of various kinds of metal ions.



CD Compounds	n
α-CD	4
β-CD	5
γ-CD	6

EXPERIMENTAL

Materials

α-Cyclodextrin (α-CD): A commercial product (Nakarai Chemical Ltd., Kyoto) was used; $[\alpha]_D$ 146.7° (C 0.175, H_2O).

β-Cyclodextrin (β-CD): A commercial product (Tokyo Kasei Co., Tokyo) was used after recrystallization from water; $[\alpha]_D$ 160.0° (C 0.637, H_2O).

γ-Cyclodextrin (γ-CD): A commercial product (Tokyo Kasei Co., Tokyo) was used; $[\alpha]_D$ 172.3° (C 0.140, H_2O).

Vinyl monomers: Freshly distilled MMA, BMA, St, and AN were used for the polymerization.

Metal salts: Commercial grade (Guaranteed Reagent) of magnesium chloride ($MgCl_2 \cdot 6H_2O$), manganous chloride ($MnCl_2 \cdot 4H_2O$), ferrous chloride ($FeCl_2 \cdot 4H_2O$), ferric chloride ($FeCl_3 \cdot 6H_2O$), cobaltous chloride ($CoCl_2 \cdot 6H_2O$), nickelous chloride ($NiCl_2 \cdot 6H_2O$), and cupric chloride ($CuCl_2 \cdot 2H_2O$) were used without purification.

Polymerization Procedures

A typical procedure was as follows. A mixture of an amylose, a monomer, a metal salt, and water was placed in a glass tube. The tube was replaced by nitrogen under vacuum and sealed. The polymerization was carried out with continuous shaking in a thermostat at a preset temperature. After the polymerization, the content was poured into a large amount of methanol to give the precipitated polymer. The polymer was filtered and washed well with hot water to remove the residual amylose. The resultant polymer was dried and subjected to the determination of the percent conversion by weight. The average degree of polymerization ($\bar{P}_n$) of the resulting polymer was calculated from its intrinsic viscosity in benzene.

RESULTS AND DISCUSSION

Effect of the Addition of Various Kinds of Metal Salts

The polymerization of MMA with β-CD was carried out in the presence of eight kinds of metal chlorides. The conditions for the polymerization were as follows; MMA, 3 cm^3; H_2O, 10 cm^3; β-CD, 0.1 g; metal salts, 5.87×10^{-3} mol/dm^3 (this value was estimated by considering the optimal amount of $CuCl_2 \cdot 2H_2O$ obtained from the experiment described below) at 85°C, 3 h. The results are compiled in Table 1. Table 1 reveals that the percent conversion of the polymerization in a β-CD/Cu(II) ion system is larger than that for thermal polymerization in the absence of the Cu(II) ion. However, the percent conversions by the other metal salts/β-CD systems are nearly equal to those of the respective thermal polymerizations. Furthermore, one can find in Table 1 that the Fe(III) ion accelerates polymerization while the Fe(II) ion represses polymerization. On the basis of these data, subsequent experiments were carried out mainly using $CuCl_2 \cdot 2H_2O$ and $FeCl_3 \cdot 6H_2O$ as the metal salts.

Polymerizations of MMA in the systems of β-CD/Cu(II) and β-CD/Fe(III) ions were carried out. Keeping the amounts of MMA (3 cm^3), water (10 cm^3) and β-CD (0.1 g) constant, the amount of $CuCl_2 \cdot 2H_2O$ was changed from 10^{-6} to 0.1 g. As shown in Fig. 1, the percent conversion of the polymerization increased with the increase of the amount of the metal salt, and showed a maximal value where the molar ratio of the Cu(II) ion to β-CD was about one. In the case of the β-CD/Fe(III) ion system, the same trends were also observed (see Fig. 1). Moreover, the percent conversion was then drastically decreased with the increase of the amount of the metal salts added beyond the optimal amount. This result may be attributed to the fact that a radical (R·) initially formed is readily captured by

TABLE 1. Effect of Various Kinds of Metal Salts on β-CD/Metal Ion Systems[a]

Salts	β-CD (g)	Conversion (%)
$MgCl_2 \cdot 6H_2O$	0	0.98
	0.1	1.20
$MnCl_2 \cdot 4H_2O$	0	0.88
	0.1	0.26
$FeCl_2 \cdot 4H_2O$	0	0.47
	0.1	0.23
$CoCl_2 \cdot 6H_2O$	0	1.37
	0.1	0.84
$NiCl_2 \cdot 6H_2O$	0	1.02
	0.1	1.13
$CuCl_2 \cdot 2H_2O$	0	0.64
	0.1	2.37
$FeCl_3 \cdot 6H_2O$	0	1.72
	0.1	2.50

[a] Polymerization conditions: MMA, 3 cm^3; salts, 5.87×10^{-3} mol/dm^3; H_2O, 10 cm^3; 85°C; 3 h.

the metal cation (see Eq. 1), as discussed in the studies of the polymerization of MMA in the system of starch or cellulose/metal salts [1d, 4, 5].

$$R\cdot + CuCl_2 \longrightarrow RCl + CuCl \qquad (1)$$

As shown in Fig. 1, the average degree of polymerization ($\bar{P}_n$) for the poly-MMA obtained from the polymerization in the β-CD/Cu(II) ion system was found to decrease gradually with the increase of the amount of the Cu(II) ion used.

The polymerizations of MMA were also carried out in the systems of α-CD/Cu(II) and γ-CD/Cu(II) ions. The results, which are illustrated graphically in Fig. 2, indicate that both systems can also serve as initiators in a similar fashion in the case of the β-CD/Cu(II) ion system.

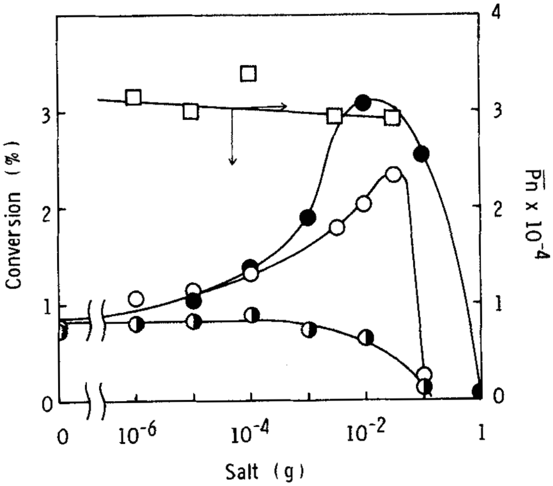


FIG. 1. Effect of the amount of metal salts. MMA, 3 cm^3, H_2O, 10 cm^3; β-CD, 0.1 g; $CuCl_2 \cdot 2H_2O$ (○); $FeCl_3 \cdot 6H_2O$ (●); thermal polymerization [$CuCl_2 \cdot 2H_2O$] (◑); $\overline{P}_n$ [β-CD/Cu(II) ion system] (□); 85°C; 3 h.

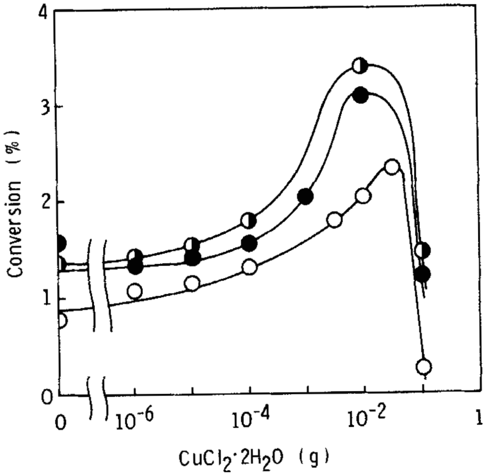


FIG. 2. Effect of the amount of $CuCl_2 \cdot 2H_2O$ on the polymerization in the systems of α-CD/Cu(II) ion, β-CD/Cu(II) ion, and γ-CD/Cu(II) ion. MMA, 3 cm^3; H_2O, 10 cm^3; CD compounds, 0.1 g; 85°C; 3 h; α-CD (●); β-CD (○); γ-CD (◑).

TABLE 2. Polymerization of Vinyl Monomers in the β-CD/Cu(II) Ion System[a]

Monomer	$CuCl_2 \cdot 2H_2O$ (g)	β-CD (g)	Conversion (%)
MMA	0	0	0.88
	0.01	0	0.64
	0.01	0.1	2.37
BMA	0	0	1.61
	0.01	0	2.53
	0.01	0.1	4.81
St	0	0	2.29
	0.001	0	2.35
	0.001	0.1	2.38
AN	0	0	0
	0.01	0	4.42
	0.01	0.1	1.43

[a] Polymerization conditions: Monomer, 3 cm^3; H_2O, 10 cm^3; 85°C; 3 h.

Polymerization of Various Vinyl Monomers

The results for the polymerizations of various kinds of vinyl monomers in the β-CD/Cu(II) ion system are summarized in Table 2. This system can accelerate the polymerization of MMA and BMA. However, the acceleration is not observed in the polymerizations of AN and St. The percent conversions for the polymerizations of MMA and BMA by the β-CD/Cu(II) ion system are about threefold larger than those for their thermal polymerizations.

Effect of the Amount of β-CD

Keeping the amounts of MMA (3 cm^3), H_2O (10 cm^3), and $CuCl_2 \cdot 2H_2O$ (0.1 g) constant, the amount of β-CD was changed. As shown in Fig. 3, the percent conversion increased with the increase of the amount of β-CD, and became almost constant in the region where the molar ratio of $CuCl_2 \cdot 2H_2O$ to β-CD($CuCl_2 \cdot 2H_2O$/β-CD) is beyond ~1.

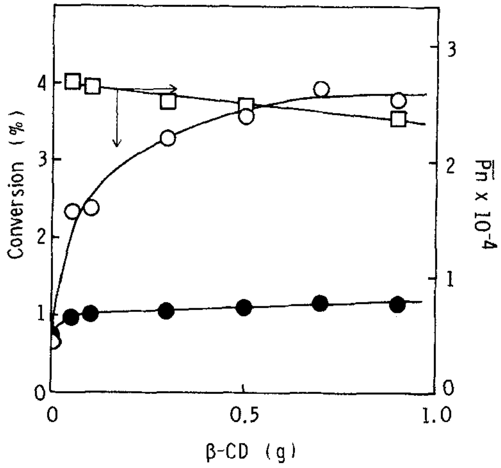


FIG. 3. Effect of the amount of β-CD. MMA, 3 cm^3; H_2O, 10 cm^3, $CuCl_2 \cdot 2H_2O$, 0 g (●); 0.01 g (○); $\overline{P}_n$ [β-CD/Cu(II) ion system] (□); 85°C; 3 h.

Effect of the Amount of Water

In analogy with the starch or cellulose/metal ion system [1c], the polymerization of MMA in the system of β-CD/Cu(II) ion was affected by the amount of water added. As shown in Fig. 4, when the amount of water was changed, keeping the amounts of MMA (3 cm^3), $CuCl_2 \cdot 2H_2O$ (0.01 g), and β-CD (0.1 g) constant, the percent conversion increased with the increase of the amount of water, and became almost constant when more than 6 cm^3 of water was added.

Effect of the Amount of MMA

The correlation of the corrected polymer yield for the polymerization of MMA in the β-CD/Cu(II) ion system with the amount of MMA was determined. As shown in Fig. 5, a linear relationship was not observed between the polymer yield and the amount of MMA, in contrast to the polymerization initiated by ordinary radical initiators. The polymer yield became almost constant in the region of over 3 cm^3 of MMA.

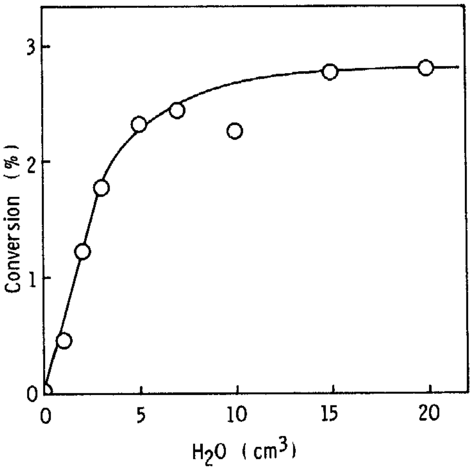


FIG. 4. Effect of the amount of water. MMA, 3 cm^3 ; $CuCl_2 \cdot 2H_2O$, 0.01 g; β-CD, 0.1 g; 85°C; 3 h.

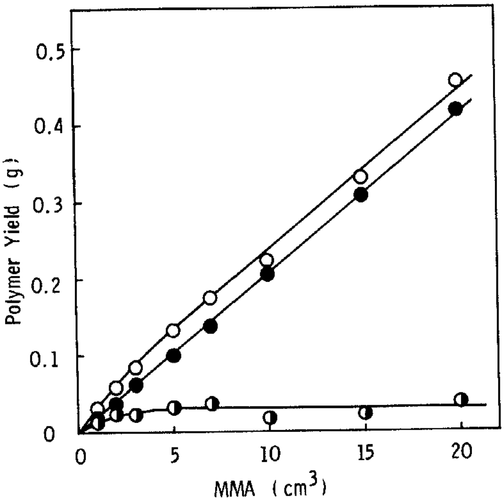


FIG. 5. Effect of the amount of MMA. H_2O, 10 cm^3, $CuCl_2 \cdot 2H_2O$, 0.01 g; β-CD, 0 g; (●); 0.1 g (○); corrected yield (◑); 85°C; 3 h.

TABLE 3. Effect of Radical Scavengers[a]

Inhibitor	Conversion (%)
-	2.37
DPPH	0
HQ	trace
TPV	0.22
t-BC	0.35

[a] Polymerization conditions: MMA, 3 cm^3; H_2O, 10 cm^3; β-CD, 0.1 g; inhibitor, 0.1 g; $CuCl_2 \cdot 2H_2O$, 0.01 g; 85°C; 3 h.

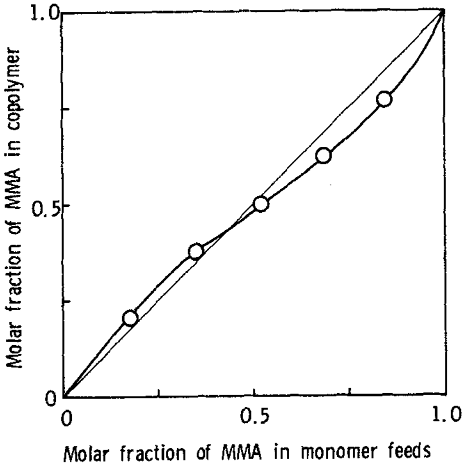


FIG. 6. Result of the copolymerization of MMA and St in the β-CD/Cu(II) ion system. Monomer total volume, 3 cm^3; β-CD, 0.1 g; $CuCl_2 \cdot 2H_2O$, 0.01 g; H_2O, 10 cm^3; 85°C; 3 h.

Effect of Radical Scavenger and Copolymerization of MMA and St

The polymerization of MMA in the β-CD/Cu(II) ion system was carried out in the presence of several radical scavengers, such as 1,1-diphenylpicrylhydrazyl (DPPH), hydroquinone (HQ), 1,3,5-triphenylverdazyl (TPV), and t-butylcatechol (t-BC). The results obtained are summarized in Table 3. As shown in Table 3, polymerization is inhibited in the presence of radical scavengers.

Moreover, the copolymerization of MMA and St in the β-CD/Cu(II) ion system was also carried out. As shown in Fig. 6, an inverse sigmoid curve was observed. These results indicate that polymerization in the present system should proceed through a radical mechanism.

In summary, the present polymerization requires a certain metal ion, such as Cu(II) or Fe(III), and water, together with the cyclodextrin compounds. In the β-CD/Cu(II) ion system, the highest percent conversion has been obtained where the molar ratio $CuCl_2 \cdot 2H_2O/\beta$-CD is about one. Moreover, the polymerization seems to proceed through a radical mechanism. These results are similar to those for the polymerization of MMA in the system of starch or cellulose/metal ions. Therefore, it may be considered that the initiation mechanism in the cyclodextrin/metal ion systems is the same as that in the starch or cellulose/metal ion systems reported by Imoto et al. [2]. However, the cyclodextrin/metal ion systems resulted in a lower percent conversion than the starch or cellulose/metal ion systems. We now think that this is due to the magnitude of the hydrophobic area formed by the polysaccharides in water. In the cases of starch and cellulose, the intermolecular and intramolecular interactions of the long-chain polysaccharides have been known to form a large hydrophobic area which favors inclusion of a large quantity of the vinyl monomer [2]. The cyclodextrin compounds possess a small hydrophobic area which can perhaps incorporate one molecule of the vinyl monomer. The differences in magnitudes of the incorporation abilities toward the vinyl monomers between the two kinds of systems should reflect the rate of polymerization. However, the mechanistic implications of the present polymerization are not yet clear. They will be the subject of a forthcoming paper in this series.

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